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(54) Title: FUEL ADDITIVE COMPOSITION

(57) Abstract

A homogeneous fuel additive composition which comprises: (a) a dispersant comprising a hydrocarbyl poly (oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1000 to about 3000; (b) an injection detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins; (c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and (d) a natural or synthetic carrier fluid.

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FUEL ADDITIVE COMPOSITION

BACKGROUND OF THE INVENTION

Numerous deposit-forming substances are inherent in hydrocarbon fuels. These substances when used in internal combustion engines tend to form deposits on and around constricted areas of the engine contacted by the fuel. Typical areas commonly and sometimes seriously burdened by the formation of deposits include carburetor air bleeds, the throttle body and venturies, engine intake valves and ports, fuel injection nozzles, cylinder head and piston top combustion chamber surfaces, etc.

Deposits adversely affect the operation of vehicles using hydrocarbon fuels. For example, deposits on the carburetor throttle body and venturies increase the fuel-to-air ratio of the gas mixture to the combustion chamber thereby increasing the amount of unburned hydrocarbon and carbon monoxide discharged from the chamber. High fuel-to-air ratios also reduce the gas mileage obtainable from the vehicle.

Deposits on the engine intake valves that are sufficiently heavy, restrict the gas mixture flow into the combustion chamber. This restriction starves the engine of air and fuel and results in a loss of power. Deposits on the valves also increase the probability of valve failure due to burning and improper valve seating. In addition, these deposits may break off and enter the combustion chamber possibly resulting in mechanical damage to the piston top, piston rings, cylinder head, etc.

It has long been known that the formation of these deposits can be inhibited as well as removed by incorporating an active detergent into the fuel. These detergents function to cleanse these deposit-prone areas of the harmful deposits, thereby enhancing engine performance and longevity.

The first generation of fuel additives consisted of detergents which helped to maintain the cleanliness of critical carburetor elements. These initial fuel additives were typically used in small doses, generally in the range of 15 to 30 ppm. Unfortunately, these small doses of additive provided little deposit control in other parts of combustion engines.

The next generation of fuel additives generally provided improved deposit control in the intake system including intake manifold hotspots, runners, intake valve ports, and intake valves. The extent of deposit control was typically modulated by controlling additive dose, usually in the range of 70 to 2,000 ppm. However, as additive doses increased to high levels, the accumulation of combustion chamber deposits became a significant problem for reasons which will become apparent hereinbelow.

In recent years the wide-spread use of non-leaded gasoline has further complicated the use of detergent-type gasoline additives. In automobile engines that require the use of non-leaded gasolines (to prevent disablement of catalytic converters used to reduce emissions), it has been found difficult to provide gasoline of sufficient octane to prevent knocking and the concomitant damage which it causes. The problem arises from an octane requirement increase,

herein called "ORI", which results from deposits formed by the use of commercial gasolines.

The basis of the ORI problem is as follows: each engine, when new, requires a certain minimum octane fuel in order to operate satisfactorily without pinging and/or knocking, and/or after run. As the engine is operated on any gasoline, this minimum octane requirement increases. This is apparently caused by formation of deposits in the combustion chamber. In most cases, if the engine is operated on the same fuel for a prolonged period, the ORI will reach an equilibrium. Equilibrium is typically reached after 5,000 to 15,000 miles of automobile operation.

The octane requirement increase in a particular engine used with commercial gasolines will vary at equilibrium from 4 to 6 octane units to as high as 12 or 15 units, depending upon the gasoline compositions, engine design and type of operation. The seriousness of the problem is thus apparent. A typical automobile with a research octane requirement of 85, when new, may after a few months of operation require 97 research octane gasoline for proper operation, and little unleaded gasoline of that octane is available. The ORI problem also exists to some degree with engines operated on leaded fuels. U.S. Patent Nos. 3,144,311; 3,146,203; and 4,247,301 disclose lead-containing fuel compositions having reduced ORI properties.

The ORI problem is compounded by the fact that the most common method for increasing the octane rating of unleaded gasoline is to increase its aromatic content. These aromatics, however, eventually cause an even greater increase in the octane requirement. Moreover, some of the nitrogen-containing compounds presently used as deposit-control

additives and their mineral oil or polymer carriers may also significantly contribute to ORI in engines using unleaded fuels.

It is, therefore, particularly desirable to provide deposit control additives at doses sufficient to effectively control the deposits in intake systems of engines without themselves significantly contributing to the ORI problem.

In this regard, the hydrocarbyl poly(oxyalkylene) aminocarbamate dispersants are commercially successful fuel additives which control induction system deposits without significantly contributing to the ORI problem. However, these additives are relatively expensive and this discourages their use in high concentrations.

At economical fuel concentrations, the hydrocarbyl poly(oxyalkylene) aminocarbamates are not quite as effective at controlling deposits in the injectors or carburetor of modern combustion engines. The performance of these engines, which contain fuel injection fuel delivery systems, can be substantially upset by relatively small amounts of deposits.

On the other hand, low molecular weight hydrocarbyl amine and polyamine detergents are known to effectively control deposits in injectors. These amine detergents are similar to those described earlier that were used to maintain clean carburetors. However, to control deposits on injectors, these detergents are used at fuel concentrations in the range of 40 to 70 ppm. It is now known that such high doses of injector detergents negatively impact the control of deposits on intake valves and in the combustion chamber of engines.

An additional problem with some low molecular weight hydrocarbyl amine and polyamine detergents that contain a primary or secondary amine functionality is the formation of a solid precipitate when the amine is exposed to carbon dioxide, such as exposure to the carbon dioxide in air. It is believed that this precipitate is a carbamic acid adduct formed by reaction of the primary or secondary amine with carbon dioxide. Whatever its chemical structure, formation of such a precipitate is undesirable for reasons which will be explained hereinbelow.

A further problem associated with some low molecular weight amines, particularly those containing polar substituents such as hydroxy groups, is the fact that these amines have a high water solubility, and therefere, on contact with water, can be completely extracted out of the hydrocarbon phase and into the water phase. As a result, such amines would have reduced effectiveness in hydrocarbon fuels.

In this regard, U.S. Patent No. 4,810,263 to Zimmerman et al. discloses an additive package for reducing and/or preventing fouling in a multiport fuel-injected engine which contains an amine oxide, such as bis(2-hydroxy ethyl) cocamine oxide, and a demulsifier comprising one or more demulsifying agents selected from a fatty acid alkylamine reaction product and a solution of oxyalkylated alkylphenol formaldehyde resins and polyglycols. U.S. Patent No. 4,836,829 to Zimmerman et al discloses a similar additive package which contains a tertiary amine, such as bis(2-hydroxy ethyl) cocamine, preferably in combination with an amine oxide, and a demulsifying agent. As noted in U.S. Patent No. 4,810,263, the amine oxide typically has water present from the manufacturing process, which is difficult to completely remove. As a result, the amine

oxide is commercially available as an isopropyl alcohol solution which contains from 6 to 8 weight percent water.

Frequently, mineral oil carriers are used with either the amine detergents or the hydrocarbyl poly(oxyalkylene) aminocarbamate dispersants to assist in removing and preventing deposits. However, even with the addition of mineral oil carriers, neither group of fuel additives provides complete intake system deposit control.

It would, therefore, be particularly desirable to combine an intake valve and combustion chamber deposit control additive, such as a hydrocarbyl poly(oxyalkylene) aminocarbamate dispersant, with an injector detergent, such as a low molecular weight amine or polyamine, and an effective amount of a carrier fluid to provide a multi-component, multi-functional fuel additive package which maximizes effective control of deposits throughout the entire intake system and combustion chamber of engines, and which itself does not significantly contribute to the octane requirement increase problem.

The choice of components for a multi-component, multi-functional deposit control fuel additive composition is not straightforward. The composition must provide effective deposit control at additive levels which are economical, and with additives which do not contribute to ORI. It is also essential that the composition remains homogeneous, i.e., a single liquid phase, under all field conditions, if the composition is to dependably deliver the expected deposit control performance when blended with fuel and in actual engine service.

In providing an effective fuel additive composition, maintaining a single liquid phase is critical. Typically, there are no practical means to re-homogenize an additive composition once distributed to the field. If the bulk additive composition separates into two or more phases, as a result of component incompatibility, neither phase will contain the effective combination of components intended for the fuel. Therefore, the overall deposit control performance of the fuel will be seriously degraded. Furthermore, the composition of additive delivered to the fuel will be erratic.

The phase separation of an incompatible composition can take many forms. Typically, the phase separation appears first as a haze which eventually settles out, either up or down, depending on the relative densities of the two phases. Thus as the level of additive in, for example, a storage tank is drawn down, the interface between the phases may pass below the liquid draw point, at which time the composition of additive flowing into the fuel will change, perhaps drastically.

A phase separation will also cause serious problems in the additive distribution system which distributes the additive composition to the fuel. If the phase separation involves two liquid phases, the heavier phase will collect on the bottom of the additive storage tank and at the low points of the additive delivery lines. This will result in the need for expensive and inconvenient periodic cleanout of the additive distribution equipment.

If the phase separation involves a solid separating from the bulk liquid additive composition, the effect would be more serious and immediate. Virtually all additive injection

systems have fine-mesh filters to protect the valves and seals in the injection pump. A solid phase would rapidly plug these filters and shut down the injector, thus requiring that the filter be cleaned before restarting the injector. A separate solid phase would also require the periodic cleaning of the additive storage tank. The criticality of a homogeneous additive composition is thus apparent.

It is generally considered beneficial to include a minor amount of a material which has fuel/water demulsifier properties in fuel blends of additive compositions. The demulsifier must exhibit demulsification properties when utilized in motor fuels at relatively low levels, such as 5 to 25 parts per million. However, it has been observed that even low dosages of such material can, in certain instances, have a negative effect on the deposit-inhibiting properties of the additive composition. Consequently, it is desirable to choose a demulsifier which does not exhibit this negative effect. In addition, it is critical that the demulsifier remain homogeneous with the additive composition for reasons cited hereinabove.

It is also generally beneficial to include a solvent or diluent in the additive composition. The primary function of this component is to reduce the low-temperature viscosity of the composition. The solvent must however be compatible with the additive components and economical.

Relevant Art

U.S. Patent Nos. 4,160,648 and 4,191,537 disclose hydrocarbyl poly(oxyalkylene) aminocarbamates as fuel additives. The use of a fuel-soluble carrier oil and,

additionally, a demulsifier in combination with the hydrocarbyl poly(oxyalkylene) aminocarbamates is also disclosed.

The use of hydrocarbyl amines and hydrocarbyl polyamines as fuel additives is disclosed in U.S. Patent Nos.:

3,438,757;	3,898,056; and
3,565,804;	3,960,515
3,574,576	

U.S. Patent Nos. 3,898,056 and 3,960,515 disclose a mixture of high and low molecular weight hydrocarbyl amines used as detergents and dispersants at low concentrations in fuels. The high molecular weight hydrocarbyl amine contains at least one hydrocaryl group having a molecular weight from about 1,900 to 5,000 and the low molecular weight hydrocarbyl amine contains at least one hydrocarbyl group having a molecular weight from about 300 to 600. The weight ratio of low molecular weight amine to high molecular weight amine in the mixture is maintained between about 0.5:1 and 5:1.

While these references disclose hydrocarbyl poly(oxyalkylene) aminocarbamates useful as dispersants and hydrocarbyl amines and polyamines useful as detergents, none of these references teach a homogeneous additive composition comprising a dispersant, detergent, carrier oil and demulsifier which, when mixed with fuel at low concentrations, provides effective deposit control throughout the entire intake system while minimizing contribution to the ORI problem.

SUMMARY OF THE INVENTION

The present invention provides a novel homogeneous fuel additive composition which comprises:

(a) a dispersant comprising a hydrocarbyl poly(oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1,000 to about 3,000;

(b) an injector detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins;

(c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and

(d) a natural or synthetic carrier fluid.

The present invention further provides a fuel composition comprising a hydrocarbon boiling in the gasoline or diesel range and from about 400 to 1,200 parts per million of the homogeneous fuel additive composition described above.

The present invention is also concerned with a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of 150° to 400°F and from about 5 to 50 weight percent of the homogeneous fuel additive composition of the invention.

Among other factors, the present invention is based on the surprising discovery that the unique combination of

dispersant, low molecular weight injector detergent, demulsifier and carrier fluid described herein provides complete intake deposit control while minimizing debilitating combustion chamber deposits, which correlate to ORI.

In addition, the use of a low molecular weight branched chain hydrocarbyl amine as an injector detergent avoids the precipitation problem associated with known amine detergents, such as oleyl amine.

DETAILED DESCRIPTION OF THE INVENTION

In essence, the present invention addresses the problem associated with the fact that none of the prior art fuel additives can singly, or in typical use concentration combinations, provide complete gasoline intake system deposit control. The instant invention demonstrates a new formulating technology which provides maximum deposit control in each critical deposit forming area while at the same time minimizing the doses of each critical ingredient. As a consequence, it is now possible to minimize the negative impact of each individual ingredient upon overall intake system and combustion chamber deposit control performance.

The instant invention describes a fuel additive composition which provides a homogeneous mixture of deposit control additives and carrier fluid, in individual proportions significantly below the levels historically recognized for maintaining adequate intake system deposit control in their respective areas of effectiveness, and an oil compatible demulsifier.

Accordingly, the novel fuel additive composition of the present invention is a homogeneous mixture which comprises the following components:

(a) a dispersant comprising a hydrocarbyl poly(oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1,000 to about 3,000;

(b) an injector detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins;

(c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and

(d) a natural or synthetic carrier fluid.

In general, the homogeneous fuel additive composition of the invention will contain about 10 to 70 weight percent of the aminocarbamate dispersant, about 1 to 10 weight percent of the hydrocarbyl amine injector detergent, about 0.5 to 5 weight percent of the fuel demulsifier and about 25 to 80 weight percent of the carrier fluid. Although the present fuel additive composition can be used neat, it is often desirable to dilute the composition with an inert solvent or diluent, up to about 50 percent dilution.

The Dispersant

The dispersant employed in the homogeneous fuel additive composition of the invention is a hydrocarbyl

poly(oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1,000 to 3,000. Thus the dispersant employed can be said to contain a poly(oxyalkylene) component, an amine component and a carbamate connecting group.

A. <u>The Poly(oxyalkylene) Component</u>

The hydrocarbyl-terminated poly(oxyalkylene) polymers which are utilized in preparing the carbamates of the present invention are monohydroxy compounds, e.g., alcohols, often termed monohydroxy polyethers, or polyalkylene glycol monocarbyl ethers, or "capped" poly(oxyalkylene) glycols, and are to be distinguished from the poly(oxyalkylene) glycols (diols), or polyols, which are not hydrocarbyl-terminated, i.e., are not capped. The hydrocarbyl-terminated poly(oxyalkylene) alcohols are produced by the addition of lower alkylene oxides, such as oxirane, ethylene oxide, propylene oxide, butylene oxide, etc. to the hydroxy compound, ROH, under polymerization conditions, wherein R is the hydrocarbyl group which caps the poly(oxyalkylene) chain. In the poly(oxyalkylene) component employed in the present invention, the group R will generally contain from 1 to about 30 carbon atoms, preferably from 2 to about 20 carbon atoms and is preferably aliphatic or aromatic, i.e., an alkyl or alkyl phenyl wherein the alkyl is a straight or branched-chain of from 1 to about 24 carbon atoms. More preferably, R is alkylphenyl wherein the alkyl group is a branched-chain of 12 carbon atoms, derived from propylene tetramer, and commonly referred to as tetrapropenyl. The oxyalkylene units in the poly(oxyalkylene) component preferably contain from 2 to about 5 carbon atoms but one or more units of a

larger carbon number may also be present. The poly(oxyalkylene) component employed in the present invention is more fully described and exemplified in U.S. Patent No. 4,191,537, the disclosure of which is incorporated herein by reference.

Although the hydrocarbyl group on the hydrocarbyl poly(oxyalkylene) component will preferably contain from 1 to about 30 carbon atoms, longer hydrocarbyl groups, particularly longer chain alkyl phenyl groups, may also be employed.

For example, alkylphenyl poly(oxyalkylene) aminocarbamates wherein the alkyl group contains at least 40 carbon atoms, as described in U.S. Patent No. 4,881,945 to Buckley, are also contemplated for use in the present invention. The alkyl phenyl group on the aminocarbamates of U.S. Patent No. 4,881,945 will preferably contain an alkyl group of 50 to 200 carbon atoms, and more preferably, an alkyl group of 60 to 100 carbon atoms. The disclosure of U.S. Patent No. 4,881,945 is incorporated herein by reference.

B. <u>The Amine Component</u>

The amine moiety of the hydrocarbyl-terminated poly(oxyalkylene) aminocarbamate is preferably derived from a polyamine having from 2 to about 12 amine nitrogen atoms and from 2 to about 40 carbon atoms. The polyamine is preferably reacted with a hydrocarbyl poly(oxyalkylene) chloroformate to produce the hydrocarbyl poly(oxyalkylene) aminocarbamate fuel additive finding use within the scope of the present invention. The chloroformate is itself derived from hydrocarbyl

poly(oxyalkylene) alcohol by reaction with phosgene. The polyamine, encompassing diamines, provides the product poly(oxyalkylene) aminocarbamate with, on the average, at least about one basic nitrogen atom per carbamate molecule, i.e., a nitrogen atom titratable by strong acid. The polyamine preferably has a carbon-to-nitrogen ratio of from about 1:1 to about 10:1. The polyamine may be substituted with substituents selected from hydrogen, hydrocarbyl groups of from 1 to about 10 carbon atoms, acyl groups of from 2 to about 10 carbon atoms, and monoketone, monohydroxy, mononitro, monocyano, alkyl and alkoxy derivatives of hydrocarbyl groups of from 1 to 10 carbon atoms. It is preferred that at least one of the basic nitrogen atoms of the polyamine is a primary or secondary amino nitrogen. The polyamine component employed in the present invention has been described and exemplified more fully in U.S. Patent No. 4,191,537.

Hydrocarbyl, as used in describing the hydrocarbyl poly(oxyalkylene) and amine components used in this invention, denotes an organic radical composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl. Preferably, the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic unsaturation. The more preferred polyamine finding use within the scope of the present invention is a polyalkylene polyamine, including alkylene-diamine, and including substituted polyamines, e.g., alkyl and hydroxyalkyl-substituted polyalkylene polyamine. Preferably, the alkylene group contains from 2 to 6 carbon atoms, there being preferably from 2 to 3 carbon atoms between the nitrogen atoms. Examples of

such polyamines include ethylenediamine, diethylene triamine, triethylene tetramine, di(trimethylene) triamine, dipropylene triamine, tetraethylene pentamine, etc. Among the polyalkylene polyamines, polyethylene polyamine and polypropylene polyamine containing 2-12 amine nitrogen atoms and 2-24 carbon atoms are especially preferred and in particular, the lower polyalkylene polyamines, e.g., ethylenediamine, diethylene triamine, propylene diamine, dipropylene triamine, etc., are most preferred.

C. The Aminocarbamate

The poly(oxyalkylene) aminocarbamate fuel additive used in compositions of the present invention is obtained by linking the amine component and the poly(oxyalkylene) component together through a carbamate linkage, i.e.,

$$-O-C(O)-\overset{|}{N}-.$$

wherein the oxygen may be regarded as the terminal hydroxyl oxygen of the poly(oxyalkylene) alcohol component, and the carbonyl group -C(O)-, is preferably provided by a coupling agent, e.g., phosgene. In the preferred method of preparation, the hydrocarbyl poly(oxyalkylene) alcohol is reacted with phosgene to produce a chloroformate and the chloroformate is reacted with the polyamine. The carbamate linkages are formed as the poly(oxyalkylene) chains are bound to the nitrogen of the polyamine through the oxycarbonyl group of the chloroformate. Since there may be more than one nitrogen atom of the polyamine which is capable of reacting with the chloroformate, the aminocarbamate contains at least one hydrocarbyl poly(oxyalkylene)

polymer chain bonded through an oxycarbonyl group to a nitrogen atom of the polyamine, but the carbonate may contain from 1 to 2 or more such chains. It is preferred that the hydrocarbyl poly(oxyalkylene) aminocarbamate product contains on the average, about 1 poly(oxyalkylene) chain per molecule (i.e., is a monocarbamate), although it is understood that this reaction route may lead to mixtures containing appreciable amounts of di or higher poly(oxyalkylene) chain substitution on a polyamine containing several reactive nitrogen atoms. A particularly preferred aminocarbamate is alkylphenyl poly(oxybutylene) aminocarbamate, wherein the amine moiety is derived from ethylene diamine or diethylene triamine. Synthetic methods to avoid higher degrees of substitution, methods of preparation, and other characteristics of the aminocarbamates used in the present invention are more fully described and exemplified in U.S. Patent No. 4,191,537.

The Injector Detergent

The injector detergent employed in the homogeneous fuel additive composition of the present invention is a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, and wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins.

In the amine injector detergent, the branched-chain hydrocarbyl group will ordinarily be prepared by polymerizing olefins of from 2 to 6 carbon atoms (ethylene being copolymerized with another olefin so as to provide a branched-chain). The branched chain hydrocarbyl group will generally have at least 1 branch per 6 carbon atoms along

the chain, preferably at least 1 branch per 4 carbon atoms along the chain and, more preferably, at least 1 branch per 2 carbon atoms along the chain. The preferred branched-chain hydrocarbyl groups are polypropylene and polyisobutylene. The branches will usually be of from 1 to 2 carbon atoms, preferably 1 carbon atom, that is, methyl. In general, the branched-chain hydrocarbyl group will contain from about 20 to 40 carbon atoms.

In most instances, the branched-chain hydrocarbyl amines are not a pure single product, but rather a mixture of compounds having an average molecular weight. Usually, the range of molecular weights will be relatively narrow and peaked near the indicated molecular weight.

The amino component of the branched-chain hydrocarbyl amines may be either a monoamine or a polyamine. The monoamine or polyamine component embodies a broad class of amines having from 1 to 10 amine nitrogen atoms and from 2 to 40 carbon atoms with a carbon to nitrogen ratio between about 1:1 and 10:1. In most instances, the amine component is not a pure single product, but rather a mixture of compounds having a major quantity of the designated amine. For the more complicated polyamines, the compositions will be a mixture of amines having as the major product the compound indicated and having minor amounts of analogous compounds.

When the amine component is a polyamine, it will preferably be a polyalkylene polyamine, including alkylenediamine. Preferably, the alkylene group will contain from 2 to 6 carbon atoms, more preferably from 2 to 3 carbon atoms. Examples of such polyamines include ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine.

A particularly preferred branched-chain hydrocarbyl amine is polyisobutenyl ethylene diamine.

The branched-chain hydrocarbyl amine injector detergents employed in the fuel additive composition of the invention are prepared by conventional procedures known in the art. Such branched-chain hydrocarbyl amines and their preparations are described in detail in U.S. Patent Nos. 3,438,757; 3,565,804; 3,574,576; 3,848,056 and 3,960,515, the disclosures of which are incorporated herein by reference.

The Demulsifier

The demulsifier employed in the fuel additive composition of the invention is a chemical agent which, when used in relatively low concentrations in gasoline compositions, will promote the rapid coalescence of emulsified water to the point where it can be effectively removed from the bulk hydrocarbon by means of static gravity assisted separation in a quiescent storage tank. The demulsifier agent is frequently a mixture of several chemical agents which in proper combination afford the desired demulsifying characteristics. These agents are typically selected from, but are not restricted to, alkylphenol resins, polyoxyalkylene-based fluids, alkylarylsulfonates, derivatives of fatty acids, and the like. One preferred demulsifier for use in the composition of this invention is known as Tolad® T-326, a commercially available demulsifier from Petrolite Corporation, Tretolite Division, St. Louis, Missouri, which comprises a mixture of oxyalkylated alkylphenol-formaldehyde resins, polyoxyalkylene glycols, and sodium arylsulfonate in heavy aromatic naphtha.

In selecting a proper fuel/water demulsifying agent, it is important that the fuel, blended with an effective deposit control amount of a fuel additive, be able to shed water or become essentially emulsion-free within 15 to 30 minutes of its contact with an aqueous phase. The fuel additive composition of this invention, being generally regarded as a dispersant agent, also has the tendency to promote emulsion formation when gasoline compositions containing the additive composition are contacted with water. Demulsifiers, at relatively low fuel concentrations, assist in the demulsification of such emulsions and thereby help to clarify otherwise cloudy wet fuels. It is important to note that demulsifiers, when used in concentrations higher than about 25 ppm, can also promote emulsification. Hence, their dosage must be carefully regulated and adjusted to the physical/chemical characteristics of fuel compositions containing the fuel additive components. Many demulsifiers will satisfy this criterion but will nevertheless fail the criterion of compatibility with the other components of the fuel additive composition.

The Carrier Fluid

The carrier fluid employed in this invention is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the nonvolatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, synthetic polyoxyalkylene derived oils, and the like, as described, for example, in U.S. Patent No. 4,191,537 to Lewis. These carrier fluids are believed

to act as a carrier for the dispersant and detergent and to assist in removing and retarding deposits.

The carrier fluid employed in the instant invention must also be capable of forming a homogeneous mixture with the other components of the present fuel additive composition. Examples of suitable carrier fluids include Chevron Neutral Oil 500R and Chevron Neutral Oil 600P, available from Chevron U.S.A. Inc., San Francisco, California.

Fuel Compositions

The fuel additive composition of the present invention will generally be employed in a hydrocarbon distillate fuel boiling in the gasoline or diesel range. The proper concentration of this additive composition necessary in order to achieve the desired detergency and dispersancy varies depending upon the type of fuel employed, the presence of other additives, and the like. In general, however, from about 400 to 1,200 parts per million (ppm) of the instant fuel additive composition in the base fuel is needed to achieve the best results. In terms of individual components, fuel compositions containing the homogeneous fuel additive composition of the invention will generally contain about 100 to 225 ppm of the aminocarbamate dispersant, about 10 to 70 ppm of the hydrocarbyl amine injector detergent, about 5 to 25 ppm of the demulsifier and about 250 to 800 ppm of the carrier fluid.

The deposit control fuel additive composition of the present invention may also be formulated as a concentrate, using an inert, stable oleophilic organic solvent boiling in the range of about 150° to 400°F. Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene,

toluene, xylenes, or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol, and the like, in combination with hydrocarbon solvents are also suitable for use with the additive composition of the invention. In the fuel concentrate, the amount of the instant additive composition will be ordinarily at least 5 percent by weight and generally not exceed 50 percent by weight, preferably from 10 to 30 weight percent.

In gasoline fuels, other fuel additives may also be included such as antiknock agents, e.g., methylcyclopentadienyl manganese tricarbonyl, tetramethyl or tetraethyl lead, tert-butyl methyl peroxide and various oxygenates, such as methanol, ethanol and methyl t-butyl ether. Also included may be lead scavengers such as aryl halides, e.g., dichlorobenzene or alkyl halides, e.g., ethylene dibromide. Additionally, antioxidants and metal deactivators may be present.

In diesel fuels, other well-known additives can be employed such as pour point depressants, flow improvers, cetane improvers, etc.

The following examples are offered to specifically illustrate this invention. These examples and illustrations are not to be construed in any way as limiting the scope of this invention.

EXAMPLES

EXAMPLE 1

Preparation of an Aminocarbamate Dispersant Useful in this Invention

A dispersant useful in this invention was prepared in a manner similar to that described in Lewis, U.S. Patent No. 4,160,648, Examples 6-8, except that diethylene triamine was used in place of ethylene diamine. In this example, a tetrapropenyl phenol was reacted stepwise with butylene oxide, phosgene, and diethylene triamine to afford a high molecular weight tetrapropenyl poly(oxybutylene) aminocarbamate, referred to hereinbelow as a polyether amine (PEA).

EXAMPLE 2

A Hydrocarbyl Amine Injector Detergent Useful in this Invention

An injector detergent (ID) was prepared in a manner similar to that described by Honnen, U.S. Patent No. 3,438,757, Example 2. In this example, a C_{30} polyisobutene having a molecular weight of approximately 420 was reacted stepwise with chlorine and ethylene diamine to produce a polyisobutene ethylene diamine adduct.

EXAMPLE 3

Carrier Fluids Useful in this Invention

Chevron Neutral Oil 500R and Chevron Neutral Oil 600P were used as carrier fluids (CF) in the examples hereinbelow. Chevron Neutral Oil 500R is a highly refined base oil having

a pour point of -12°C (Max.) and a viscosity of 98.6 cSt at 40°C. Chevron Neutral Oil 600P is a highly refined base oil having a pour point of 10°F (-12.2°C) and a viscosity of 129.5 cSt at 37.8°C.

EXAMPLE 4

A Demulsifier Useful in this Invention

The demulsifier (D) used in these examples to illustrate the present invention was a commercially available demulsifier (from Petrolite Corporation, Tretolite Division, St. Louis, MO) identified by the manufacturer as Tolad® T-326. This demulsifier comprises a mixture of oxyalkylated alkylphenol-formaldehyde resins, polyoxyalkylene glycols, and sodium arylsulfonate (1 to 5 weight percent) in heavy aromatic naphtha (30 to 60 weight percent). Tolad® T-326 is reported to have a flash point, SFCC, of 114°F, a pour point, ASTM D-97, of 5°F, and a viscosity of 263 SUS at 60°F.

EXAMPLE 5

Demulsibility Test

The procedure described by ASTM Method D-1094 was used to test demulsibility. Here, the fuel phase and the interface are rated for clarity and for persistence of an interfacial emulsion layer. The fuel additive compositions were tested and rated numerically, on a scale from one to four. The number "one" was the highest rating for clarity, and "one" was the highest rating for persistence of an interfacial emulsion layer.

The fuel additive composition of this invention, exemplified by Sample 6A below, met the requirement of a rating of one, on both these tests.

EXAMPLE 6

Preparation of Fuel Additive Compositions

Two fuel additive compositions were prepared. 150 parts of the polyether amine of Ex. 1, 25 parts of the injector detergent of Ex. 2, 12 parts of a demulsifier, 212 parts of Chevron Solvent 25, (which is a mixture of C-9 blending aromatics available from Chevron U.S.A. Inc., San Francisco, California) and 450 parts of Chevron Neutral Oil 500R (Ex. 3) were mixed at room temperature with stirring in a 200 ml flask.

Sample 6A contained Tolad® T-326 (as described in Ex. 4) as the demulsifier. Sample 6B contained L-1562 as the demulsifier. L-1562 is a commercially available demulsifier purchased from Petrolite Corporation, St. Louis, MO. A third additive composition, Sample 6C, contained oleyl amine as the injector detergent, and is shown for comparison purposes. Oleyl amine is a low molecular weight straight chain C_{18} primary amine.

EXAMPLE 7

Compatibility Test

The compatibility test used was a modification of the procedure described by ASTM Method D-2273, except that, since a significant amount of diluent solvent (Chevron Solvent 25, a mixture of C-9 blending aromatics) was already

present in these compositions, this test was performed without further dilution. The test was performed in two parts. In Part A, the samples prepared by the procedure of Example 6 were held at ambient or room temperature (about 20-25°C) for 24 hours. Each sample was then visually inspected for a secondary phase. If a secondary phase was observed, the sample was centrifuged and the volume percent of the secondary phase determined. If no secondary phase was observed, Part B of this test was performed.

In Part B, the samples were cooled to 0°F and held at this temperature for 24 hours. Each sample was then visually inspected for a secondary phase. If a secondary phase was observed, the sample was centrifuged and the volume percent of the secondary phase determined.

The results are reported in terms of volume percent of secondary phase sediment after centrifuging, which was either a liquid, a solid or a combination. Levels of sediment (or secondary phase) that exceed 0.005 vol.% are considered unacceptable.

The fuel additive composition of this invention (Sample 6A) does not have any measurable volume percent of a secondary phase under these test conditions. However, when L-1562 was used as the demulsifier (Sample 6B), or when oleyl amine was used as the injector detergent (Sample 6C), significant and unacceptable levels of a secondary phase were observed.

Fuel Additive Composition		Vol. % Secondary Phase Part A (20-25°C)	Vol. % Secondary Phase Part B (0°F)
Sample 6A.:	150 parts PEA (Ex 1) 25 parts ID (Ex 2) 450 parts CF (Ex 3, Chevron 500R) 212 parts Chev. Sol. 25 12 parts T-326	<0.005	<0.005
Sample 6B.: (Comparative)	150 parts PEA (Ex 1) 25 parts ID (Ex 2) 450 parts CF (Ex 3, Chevron 500R) 212 parts Chev. Sol. 25 12 parts L-1562	0.75	-
Sample 6C.: (Comparative)	150 parts PEA (Ex 1) 25 parts oleyl amine 450 parts CF (Ex 3, Chevron 500R) 212 parts Chev. Sol. 25 12 parts T-326	<0.005	0.05

For Sample 6B, a liquid second phase was observed at ambient temperature showing the incompatibility of the demulsifier with the other components of the fuel additive composition.

Sample 6C, containing oleyl amine as an injector detergent, was centrifuged after cooling to 0°F and showed a small volume (0.05 vol.%) of an insoluble solid sediment. Thus it failed the criterion that sediment levels must not exceed 0.005 vol.%.

EXAMPLE 8

Intake Valve Deposit Test

An unleaded regular grade gasoline was additized with fuel additive packages of this invention such that the fuel contained the following ingredients:

8A: 150 ppm of PEA (Ex 1)
25 ppm of ID (Ex 2)
450 ppm of CF (Ex 3, Chevron 600P)
12 ppm of D (T-326)

8B: 150 ppm of PEA (Ex 1)
25 ppm of ID (Ex 2)
450 ppm of CF (Ex 3, Chevron 500R)
12 ppm of D (T-326)

The gasolines were tested for intake valve keep-clean effectiveness using a procedure which utilizes a 1981 Pontiac 2.5-liter engine mounted upon an engine test stand, and run for 90 hrs. This test simulates a type of severe field test service characterized by light load driving conditions. The effectiveness of an additive package is determined by averaging the weights of accumulated intake valve deposits obtained by the end of test, and comparing these results with those obtained using identical test conditions and the unadditized fuel. A good fuel additive package capable of complete intake system keep-clean performance will typically reduce base gasoline intake valve deposits.

Using the above test conditions, the unadditized base fuel test produced, on average, 1,090 milligrams of deposits per intake valve. The same gasoline containing a fuel additive package of this invention using Chevron Neutral Oil 600P, Example 8A, gave on average 23 milligrams of deposits per intake valve. When the above comparison was made between base fuel and an additized fuel containing Chevron Neutral Oil 500R, Example 8B, we observed an average of 299 milligrams of intake valve deposits. These results are summarized below:

Fuel Blend Containing:	Av. Deposit Wgts.
No Additive (Base Case)	1090 mg
8A	23 mg
8B	299 mg

In both 8A and 8B, the average deposit weight is well below the base case, showing the effectiveness of the fuel additive composition of the invention.

EXAMPLE 9

Octane Requirement Increase Test

This test measures the potential that any gasoline additives may have in upsetting the octane requirements of gasoline operated engines. Over time, due to the buildup of deposits in the combustion chamber, higher octane gasoline is required to minimize engine knock. Unadditized gasolines contribute a baseline level of deposits which typically require a fuel having an octane value four numbers higher than the initial fuel used to start the test in order to minimize the increasing engine knock condition. Gasoline additives contribute to this problem to different degrees, and the magnitude of this contribution can be measured by comparisons with engine tests using additized fuel. The difference of ORI observed between the tests is that additional increment of increased octane number required to further minimize engine knock and is generally referred to as the octane requirement increase attributable to the gasoline additive package itself. This value is typically referred to as the "additive ORI number".

This procedure utilizes a 1975 Toyota 2.2-liter engine mounted on an engine stand and equipped with a control system to carefully regulate test conditions and engine operating cycles. The engine is first run for fifteen hours on a relatively clean-burning, additive-free alkylate fuel. At this time, the octane requirement is determined, and the fuel is switched to a mixture of 70% unleaded regular gasoline and 30% of FCC Heavy gasoline. The FCC Heavy component is employed to increase the rate of combustion chamber deposit accumulation during this phase of the test. After 110 hours of additional engine operation, the final octane requirement measurement is made.

When tested in this manner, the fuel additive package of this invention contributed one half of one octane number more than the octane requirement observed for the unadditized fuel (Test 9A). This increase was significantly less than that observed for a commercial gasoline additive package consisting of a heavy polybutene amine made from a polybutene containing, on average, 100 carbons per molecule, and having an average molecular weight of about 1450, which is reacted stepwise with chlorine and ethylene diamine, and a large dose of carrier oil (Test 9B).

Fuel Containing:		ORI Number	Increase Over Base
Base: No Additive		4.0	0
Test 9A:	150 ppm PEA (Ex 1) 25 ppm ID (Ex 2) 600 ppm CF (Ex 3, Chevron 500R) 12 ppm D (T-326) (Ex 4)	4.5	0.5
Test 9B:	250 ppm Heavy Polybutene Amine 1000 ppm CF (Ex 3, Chevron 500R)	7.0	3.0

WHAT IS CLAIMED IS:

1. A homogeneous fuel additive composition which comprises:

(a) a dispersant comprising a hydrocarbyl poly(oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1000 to about 3000;

(b) an injection detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins;

(c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and

(d) a natural or synthetic carrier fluid.

2. The fuel additive composition according to Claim 1, wherein the hydrocarbyl group in component (a) contains from 1 to about 30 carbon atoms.

3. The fuel additive composition according to Claim 1, wherein the hydrocarbyl group in component (a) is an alkylphenyl group.

4. The fuel additive composition according to Claim 3, wherein the alkyl moiety in the alkylphenyl group is tetrapropenyl.

5. The fuel additive composition according to Claim 1, wherein the amine moiety of the aminocarbamate is derived from a polyamine having from 2 to 12 amine nitrogen atoms and from 2 to 40 carbon atoms.

6. The fuel additive composition according to Claim 5, wherein the polyamine is a polyalkylene polyamine having 2 to 12 amino nitrogen atoms and 2 to 24 carbon atoms.

7. The fuel additive composition according to Claim 6, wherein the polyalkylene polyamine is selected from the group consisting of ethylene diamine, propylene diamine, diethylene triamine and dipropylene triamine.

8. The fuel additive composition according to Claim 1, wherein the poly(oxyalkylene) moiety of component (a) is derived from C_2 to C_5 oxyalkylene units.

9. The fuel additive composition according to Claim 1, wherein the hydrocarbyl poly(oxyalkylene) aminocarbamate of component (a) is an alkylphenyl poly(oxybutylene)aminocarbamate, wherein the amine moiety is derived from ethylene diamine or diethylene triamine.

10. The fuel additive composition according to Claim 1, wherein the branched-chain hydrocarbyl moiety of component (b) is polypropenyl or polyisobutenyl.

11. The fuel additive composition according to Claim 1, wherein the amine group of the branched-chain hydrocarbyl amine of component (b) is selected from the group consisting of ethylene diamine, diethylene

triamine, triethylene tetramine and tetraethylene pentamine.

12. The fuel additive composition according to Claim 1, wherein the branched-chain hydrocarbyl amine of component (b) is a polyisobutenyl ethylene diamine.

13. The fuel additive composition according to Claim 1, wherein component (a) is an alkylphenyl poly(oxybutylene)aminocarbamate, wherein the amine moiety is derived from ethylene diamine or diethylene triamine, and component (b) is a polyisobutenyl ethylene diamine.

14. A fuel composition comprising a hydrocarbon boiling in the gasoline or diesel range and from about 400 to about 1,200 parts per million of a homogeneous fuel additive composition comprising:

(a) a dispersant comprising a hydrocarbyl poly(oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1000 to about 3000;

(b) an injector detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins;

(c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and

(d) a natural or synthetic carrier fluid.

15. The fuel composition according to Claim 14, wherein said fuel composition contains about 100 to 225 ppm of the dispersant of component (a), about 10 to 70 ppm of the injector detergent of component (b), about 5 to 25 ppm of the demulsifier of component (c) and about 250 to 800 ppm of the carrier fluid of component (d).

16. A fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of 150° to 400°F and from about 5 to 50 weight percent of a homogeneous fuel additive composition comprising:

(a) a dispersant comprising a hydrocarbyl poly(oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1000 to 3000;

(b) an injector detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to 700, wherein the hydrocarbyl moiety is derived from polymers of C_2 to C_6 olefins;

(c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and

(d) a natural or synthetic carrier fluid.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/00934

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5) C10L 1/22
U.S.CL.: 44/329, 335, 387, 432

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	44/329, 335, 387, 432

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 3,898,056 (HONNEN) 05 MARCH 1975 Column 7 to column 9, lines 1-27.	1, and 10-16
Y	US, A, 3,960,515 (HONNEN) 01 June 1976 Column 3, lines 31-56, column 4, lines 20-26 and column 9, example 4).	1 and 10-16
A	US, A, 4,191,537 (LEWIS ET AL) 04 March 1980 Column 2, lines 37-52, column 7, lines 6 to col 8, lines 1-62 and column 10, lines 24-end).	1-9 and 13-16
Y	US, A, 4,197,409 (LILBURN) 08 April 1980 Column 7, lines 43 to column 9, lines 1-49	1-9, and 13-16
A	US, A, 4,247,301 (HONNEN) 27 January 1981 Column 2, lines 50-64 and column 8, lines 29-41	1 and 10-16
A	US, A,4,270,930 (CAMPBELL ET AL) 02 June 1981 Column 3, lines 9 to column 4, lines 1-13.	1-9 and 13-16

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
26 APRIL 1991	11 JUN 1991
International Searching Authority [1]	**Signature of Authorized Officer** NGUYEN NGOC-HO INTERNATIONAL DIVISION
ISA/US	MARGARET B. MEDLEY Ngoc Ho Nguyen

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	US, A, 4,274,837 (LILBURN) 23 June 1981 Column 7, line 44 to column 9, lines 49 and column 11, lines 24-59.	1-9 and 13-16
A	US, A, 4,288,612 (LEWIS ET AL) 08 September 1981 Column 6, line 51 to column 8, lines 1-4 and column 9, line 29 to column 10, lines 1-21	1-9 and 13-16
Y	US, A, 4,810,263 (LIMMERMAN ET AL) 07 March 1989 Column 4, lines 11-15 and 33-39	1 and 14-16
A	US, A, 4,877,416 (CAMPBELL) 31 October 1989 Column 2, lines 59 to column 3, lines 1-30	1-16

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter [1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers........., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [1], specifically:

3. ☐ Claim numbers__________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.